

Queen's University Belfast

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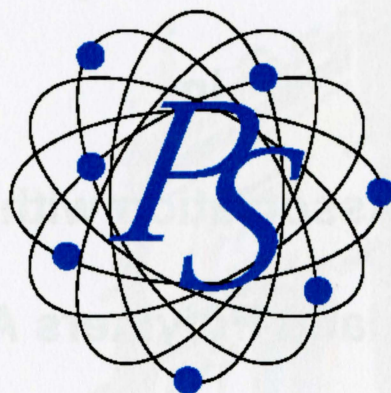
**Advanced Materials, Polymer Processing
and**

Manufacturing Conference

Tuesday 25th September 2012

Sponsor

**The organisers gratefully acknowledge sponsorship from
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Riddel Hall
Tuesday 25th September 2012

Meeting Chairman: Dr Tony McNally (QUB)

10.00-10.30: Conference Registration & (Coffee & Exhibition)

**10.30-10.45: Opening Address: Professor Sir Peter Gregson (QUB)
Chancellor Marty Meehan (U Mass Lowell)
Professor Brian MacCraith (DCU)**

Session 1

Polymer Processing

Chair – Professor Steve McCarthy (UML)

10.45-11.05: 'More for less through Simulation in Thermoforming'
Speaker: Dr Peter Martin (QUB)

11.05-11.25: 'New Extrusion Processing Method for Post Consumer Recycled Polymer Using intelligent Closed Loop Control Technology'
Speaker: Alan Clarke (PPRC, QUB)

11.25-11.45: 'Guidelines for Injection Molding of Micro and Nano-structured Surfaces'
Speaker: Professor Carol Barry (UML)

11.45-12.05: 'Future-Proofing the Rotational Moulding Process'
Speaker: Dr Mark McCourt (PPRC, QUB)

12.05-12.25: 'Modeling and Instrumentation of Stretch Blow Moulding'
Speaker: Dr Gary Menary (QUB)

12.30-13.15: Lunch & Exhibition

Session 2

Advanced Polymer Materials/Nanomaterials/Nanomanufacturing

Chair – Professor Richard O'Kennedy

13.15-13.35: 'U Mass Lowell, Nanomanufacturing : Creating a Vision for Nanomanufacturing'
Speaker: Professor Joey Mead (UML)

13.35-13.55: 'Nano-cellulose reinforced polymers: Current status and future potential'
Speaker: Professor Peter Hornsby (QUB)

13.55-14.15: 'The effect of electric current on bacterial adherence on conducting polymers'
Speaker: David Freebairn (QUB)

14.15-14.35: 'Using Nanomaterials in water and wastewater treatment'
Speaker: Dr Anne Morrissey (DCU)

14.35-14.55: 'Nanocanary™ Technologies: Cell-based biosensors to evaluate cellular response to nanomaterials, chemicals, drugs and toxins.'
Speaker: Professor Susan Braunhut (UML)

14.55-15.15: Coffee & Exhibition

Session 3

Medical Devices/Biomaterials

Chair – Professor Eileen Harkin-Jones

- 15.15-16.05: 'Biodegradable Polymers for Medical Applications'**
Speaker: Professor Steve McCarthy (UML)
- 16.05-16.25: 'Bioresorbable Implants for Orthopaedic Applications'**
Speaker: Professor Fraser Buchanan (QUB)
- 16.25-16.45: 'Porous nano-templated carbon monolithic structures and associated fabrication effects from laser ablation'**
Speaker: Dr Dermot Brabazon (DCU)
- 16.45-17.05: 'Injectable Orthopaedic Bone Cements: Advanced Mixing and Delivery Technology'**
Speaker: Dr Nicholas Dunne (QUB)
- 17.05-17.25: 'Biomedical Diagnostics: Challenges and Recent Advances'**
Speaker: Professor Richard O'Kennedy (DCU)
- 17.40-18.00: Tours of PPRC (Ashby Building)**
- From 18.45: Drinks Reception – Great Hall (Lanyon Building)**
- 19.30: Gala Dinner – Great Hall (Lanyon Building)**

(Guests of Honour: Gregory S Burton, US Consul General; Chancellor Meehan; President McCraith)

Speakers: Professor Sir Peter Gregson (QUB)
Chancellor Marty Meehan (UML)
President Brian MacCraith (DCU)

More for Less Through Simulation in Thermoforming

Peter Martin*, Ciaran O'Connor and Tony Keaney

*School of Mechanical & Aerospace Engineering
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Although thermoforming can appear to be a relatively straightforward process, its underlying principles are complex. Of the major industrial polymer processing techniques it is one of the most poorly understood and as a result processing companies are forced to avoid the perceived complexity of advanced technology by relying on trial and error methods. As a direct consequence many thermoformed products are not fully optimised meaning that their design and wall thickness distributions often contain excessive material that adds to costs. In many industries such problems have been largely overcome through the development of complex process simulators that permit virtual prototyping and the elimination of trial and error methods.

Session 1

Polymer Processing

Chair: Professor Steve McCarthy (UML)

Fig. 1 - Thermoforming Process Simulation

Our work shows how a combination of advances in new and measurement techniques, finite element modelling and simulation software have helped researchers at Queen's University to take thermoforming processes to new levels of sophistication. These include both product and process models (shown in Fig. 1) and the presentation explores the strengths and future potential of modelling through a number of case studies. In particular the work demonstrates how simulation can achieve substantial savings and can allow a processor to develop new products in the thermoforming.

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More for Less Through Simulation in Thermoforming

Peter Martin*, Ciaran O'Connor and Tony Keaney

*School of Mechanical & Aerospace Engineering
Queen's University Belfast, Northern Ireland*

Although thermoforming can appear to be a relatively straightforward process, its underlying principles are complex. Of the major industrial polymer processing techniques it is one of the most poorly understood and as a result processing companies have tended to avoid the perceived complexity of advanced technologies employed elsewhere and instead have overly relied on trial and error methods. As a direct consequence many thermoformed products are not fully optimized meaning that their design and wall thickness distributions often contain excessive material that simply adds to costs. In many industries such problems have been largely overcome through the development of complex process simulations that permit virtual prototyping and the elimination of trial and error.

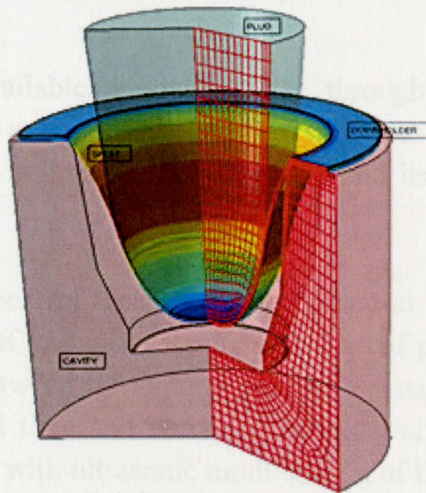


Fig. 1 –Thermoforming Process Simulation

This work shows how a combination of advances in test and measurement techniques, constitutive models and simulation software have helped researchers at Queen's University Belfast to advance models of thermoforming processes to new levels of sophistication. These include both product and process models (shown in Fig. 1) and the presentation explores the capabilities and future potential of modelling through a number case studies. In particular the work demonstrates how simulation can achieve substantial savings and can allow a processor to create more for less in thermoforming.

Keywords: Thermoforming, Simulation

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“New Processing Method for Post Consumer Recycled High Density Polyethylene Using Intelligent Closed Loop Control Technology”

Alan Clarke, Bao Kha Nguyen, Gerard McNally, Paul Beaney

Polymer Processing Research Centre, Ashby Building, Stranmillis Road, Queens University, Belfast, BT9 5AH

Keywords: Extrusion, Polymer, Post Consumer, Recycled, Closed Loop Control

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Bao Kha Nguyen, b.nguyen@qub.ac.uk

The viscosity of the melt within the extruder barrel is known to be the controlling material factor in determining the output of the extruder. In post consumer waste, the rheology of the material is not consistent and is unpredictable and this results in variable output during the process.

Commercial systems are available to maintain the throughput and the dimension of the extrudate by making changes to linespeed. This however does not consider the effect of these changes within the extruder on internal melt viscosity and its resultant effect on these same parameters.

The intelligent closed loop control technology developed at QUB maintains melt viscosity during extrusion regardless of variations in the viscosity of post consumer regrind material through maintaining ratio between throughput and melt pressure, see fig 1. The changes in viscosity are detected in real time and corrected immediately by automatically controlling screw speed and temperature with ultrasonic modification of the melt. For more information see www.peratechnology.com/case-studies/ultravisc.php

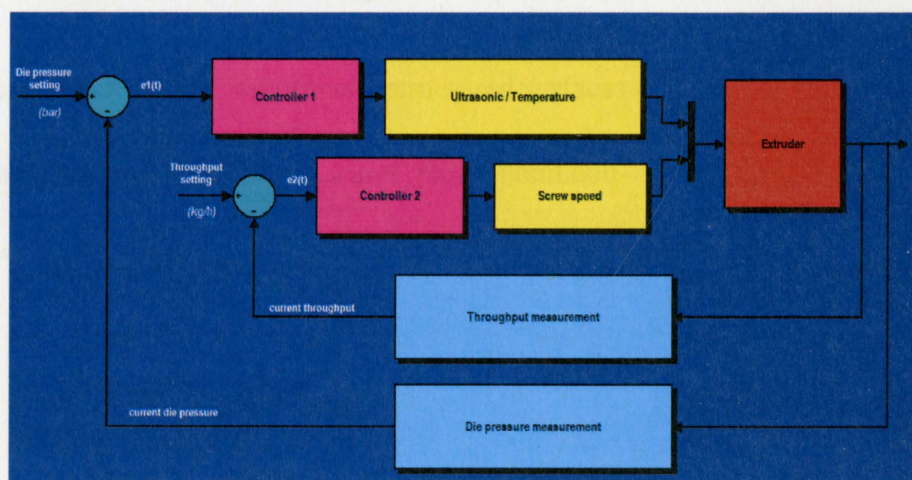


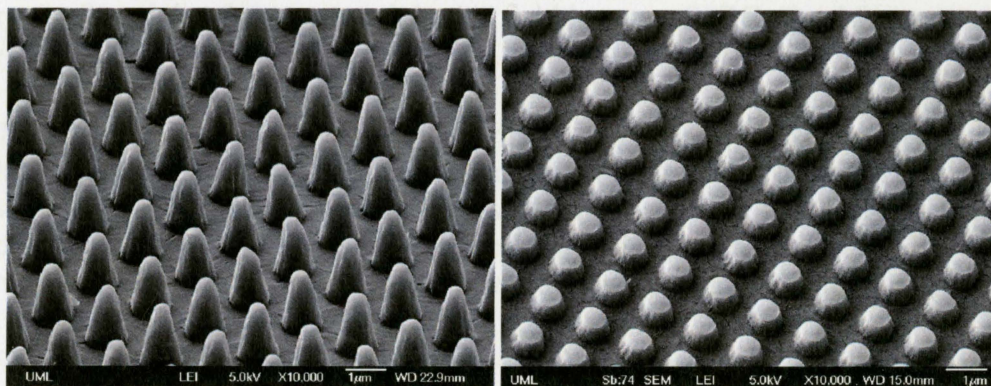
Fig 1 Schematic of Ultravisc Intelligent control System

Guidelines for Injection Molding of Micro and Nano-structured Surfaces

Carol Barry^{a*} and Joey Mead^a

^a *University of Massachusetts Lowell, 1 University Avenue, Lowell, MA, USA*

Injection molded micro and nanostructured surfaces have applications in drug delivery, drug development, analytical biochemistry, medical diagnostic (biosensor, microarrays, and assays), electronics, data storage, self-cleaning surfaces, wrinkled surfaces for optical devices and flexible electronics, patterned adhesives, and tissue scaffolds. Successful molding of these surfaces depends on understanding the changes required in product design, material selection, tool design and fabrication, and plastics processing. For example, the microscale features shown below were molded from tooling inserts fabricated by lithographic and etching processes; use of an anti-stiction coating on the tooling significantly improved filling and part ejection. The relatively high aspect ratio features were more easily reproduced with thermoplastic elastomers than with amorphous polymers like polycarbonate. Gating so that melt flowed into the features significantly enhanced feature replication (left), whereas designs where melt flowed across the features produced hesitation (right). This presentation focuses on guidelines arising from investigations of injection molding these devices.



Keywords: injection molding, nano/micro-structured surfaces

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Future Proofing the Rotational Moulding Industry

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Belfast, BT9 5AH*

Keywords: Rotomoulding, Tanks, Multi-layer, PLA, Foam

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The Polymer Process Research Centre (PPRC) at Queens University, Belfast is currently involved in a number of large collaborative rotomoulding research and development projects for Companies and Trade Associations across Europe. In a climate of high energy costs and increased competition, many of these projects are aimed specifically at 'future-proofing' the rotomoulding industry. This presentation will concentrate on the development of rotomoulding multi-layer structures and processes:

- The tightening of legislation on fuel tank permeation rates for small off-road equipment (SORE) has prompted a focus on the development of novel high-barrier, multi-layer rotomoulded structures. The presentation will highlight the collaborative research and development work in this field between PPRC, Total Petrochemicals and Arkema.
- The distinctive polymer melt characteristics of the materials developed for the multi-layer fuel tank market have in turn been further enhanced to add structural integrity to very large rotomoulded components through the use of foaming agents and polyethylene foam sandwich constructions. This is increasingly being used in the marine / boat construction industry where unique mechanical properties are required.
- Structural foam sandwich constructions have been further improved through research on new generation 'bio-polymers' and in particular polyethylene / polylactide (PLA) blends. These materials exhibit exceptional characteristics in terms of mechanical properties, service temperature and paintability. All of which are characteristics which are increasingly making the rotational moulding industry of distinct interest to the automotive sector.
- The culmination of many years research on multi-layer rotomoulding materials resulted in a major EU-funded research program aimed at improving and developing multi-layer processing methods. The results from the 'Rotoflex' FP7 project into automating multi-layer rotomoulding technology will also be presented.

Modelling and Instrumentation of Stretch Blow Moulding

G. H. Menary^{a,*}, J. Nixon^a, S. Yan, Y.M. Salomeia^b and C.G. Armstrong^a

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The injection stretch blow moulding process is used to manufacture PET containers used in the soft drinks and carbonated soft drinks industry. The process consists of a test tube like specimen known as a preform which is heated, stretch and blown into a mould to form the container. This research is focused on developing a validated simulation of the process thus enabling manufacturers to design their products in a virtual environment without the need to waste time, material and energy. The simulation has been developed using the commercial FEA package Abaqus and has been validated using state of the art data acquisition system consisting of measurements for preform temperature (inner and outer wall) using a device known as THERMOscan (Figure 1), stretch rod force and velocity, internal pressure and air temperature inside the preform using an instrumented stretch rod and the exact timing of when the preform touches the mould wall using contact sensors. In addition, validation studies have also been performed by blowing a perform without a mould and using high sped imaging technology in cooperation with an advanced digital image correlation system (VIC 3D) to provided new quantitative information on the behaviour of PET during blowing. The approach has resulted in a realistic simulation in terms of accurate input parameters, preform shape evolution and prediction of final properties.

Keywords: Blow Moulding, PET, Instrumentation

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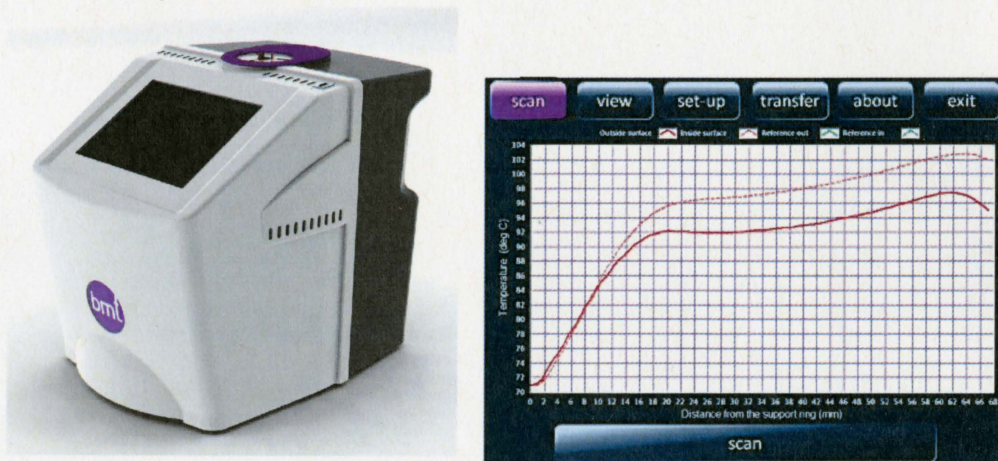


Figure 1: THERMOscan and corresponding measurement of perform temperature

UMass Lowell Nanomanufacturing: Creating a Vision for Nanomanufacturing

Jocelyn Mendez and Richard O'Kennedy

University of Massachusetts Lowell / University Avenue Lowell, MA 01854

Nanotechnology offers tremendous opportunities for novel products and materials with superior sensitivity, performance, and lighter weight, but is hampered by the lack of robust nanomanufacturing processes. Polymer materials can be processed with high rate and low cost and have a wide range of material properties, and are light in weight. They can be compounded with fillers, constructed into multi-layer films, and modified in-situ to enhance their properties, making them an excellent platform for nanomanufacturing. For example, polymer materials can be mixed with nanofillers to make nanocomposites using extremely advanced mixing processes, such as twin screw extrusion. Polymers can also be extruded into multi-layer films by layer-by-layer deposition, including barrier and piezoelectric films. Films with both barrier and piezoelectric properties can be produced. Polymers can be extruded into controlled nanostructures, such as nanowires, by directed assembly into nanostructures, multi-layer structures for biological and lab-on-a-chip applications (Figure 1b). The directed assembly of nanostructures is a promising polymer nanomanufacturing process followed by transfer to a substrate to produce structures, such as carbon nanotubes.

Section 2

Advanced Polymer Materials/Nanomaterials/Nanomanufacturing

Chair: Professor Richard O'Kennedy



Figure 1. (a) Horizontal film produced by multilayer extrusion. (b) Polymer (PE) and PMMA extruded in a single assembly process into multiple length scales.

Keywords: nanomanufacturing, polymer nanocomposites, extrusion, directed assembly.

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UMass Lowell Nanomanufacturing: Creating a Vision for Nanomanufacturing

Joey Mead^{a,*} and Carol Barry^a

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Nanoscience discoveries offer tremendous opportunities for of novel products and materials with superior sensitivity, performance, and lighter weight, but is hampered by the lack of robust nanomanufacturing processes. Polymer materials can be processed with high rate fabrication methods, have a wide range of material properties, and are light in weight. They can be compounded with fillers, coextruded into multi-layer films, and modified in roll-to-roll processes, making them an excellent platform for nanomanufacturing. For nanoscale structures, polymer materials can be mixed with nanofillers to make nanocomposites using industrially relevant melt mixing processes, such as twin screw extrusion. Polymers can also be extruded into multi-layer films for improved properties, including barrier and toughness (Figure 1a). Films with both horizontal and vertical layers can be produced. Polymer blends can be patterned into controlled micro and nanoscale morphologies by directed assembly into nonuniform, multi-scale geometries for biological and lithography applications (Figure 1b). The directed assembly of different nanoelements (e.g. conducting polymers, nanotubes) followed by transfer to a polymer can be used to fabricate structures, such as carbon nanotubes on an insulating polymer for flexible electronics. Multiple processes can be combined for making functional materials. Thus, polymers provide an exciting platform for future nanomanufacturing applications.

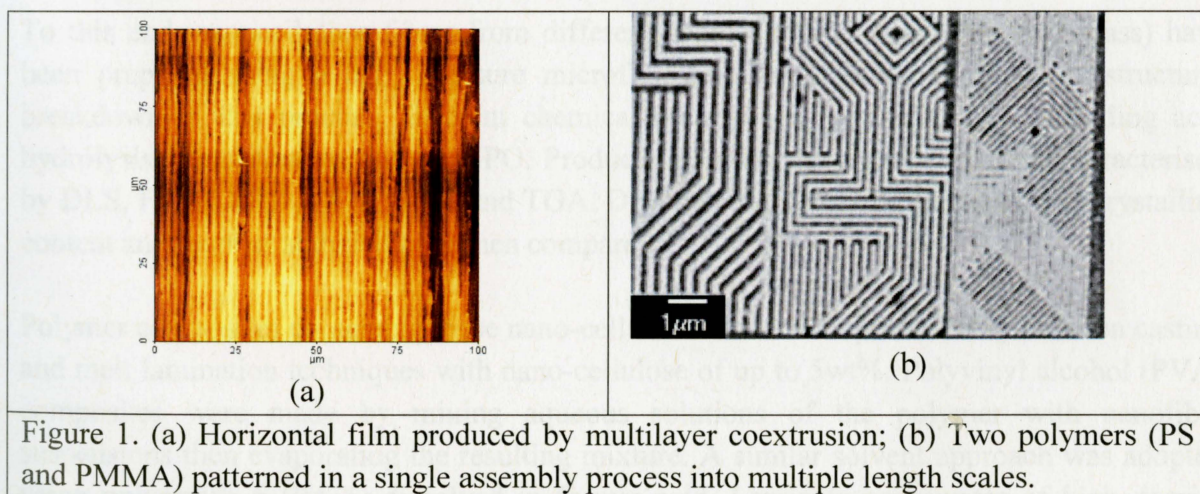


Figure 1. (a) Horizontal film produced by multilayer coextrusion; (b) Two polymers (PS and PMMA) patterned in a single assembly process into multiple length scales.

Keywords: nanomanufacturing, polymer nanocomposites, coextrusion, directed assembly.

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Nano-Cellulose Reinforced Polymers: Current Status and Future Potential

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^b *Applied Science Division, Agri-Food and Bioscience Institute, Newforge Lane, Belfast, UK*

Keywords: Cellulose nanofibres; Polymer reinforcements; Microfibrillation

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Whilst reinforcement of polymers using conventional natural fibres is well established commercially, in particular for use in the automotive industry, there is increasing interest in the use of cellulose nano-fibres derived from a variety of natural sources, which potentially have a much higher reinforcing capability than the currently used fibre feedstocks. This paper will highlight preparation methods for nano-cellulose reinforcements derived from banana tree fibres, flax and grass, based on microfibrillation and will exemplify the benefits and challenges of using them as additives in hydrophilic and hydrophobic polymers. Examples will be presented showing the influence of preparation method on the structure of the fibres and their effect on the physical properties of selected polymers, including polyethylene, poly(vinyl alcohol) and polyamide 6.

To this end, nanocellulose fibres from different sources (flax, banana tree and grass) have been prepared using a high pressure microfluidizer. To facilitate the ease of structural breakdown in this process, different chemical pretreatments were applied, including acid hydrolysis, mercerization and TEMPO. Products made by these methods were characterised by DLS, FTIR, XRD, TEM, SEM and TGA. Differences in particle size, cellulose crystalline content and thermal stability were then compared.

Polymer composites containing these nano-cellulose fibres were produced by solution casting and melt lamination techniques with nano-cellulose of up to 5wt%. Polyvinyl alcohol (PVA) composites were made by mixing aqueous solutions of the polymer with nanofibre suspensions then evaporating the resulting mixture. A similar solvent approach was adopted using polyamide 6 (PA-6) dissolved in formic acid. Laminate composites of high density polyethylene (HDPE) were made by first preparing nanocellulose paper, made by evaporation of aqueous suspensions, then melt compression within preformed sheets of the polymer of known thickness. Mechanical tests were undertaken on these composite samples in both tensile and dynamic testing modes. Further details of nano-cellulose preparation, composite preparation, testing and characterization procedures can be found in [1-3].

By way of example, Figure 1 demonstrates the reinforcing efficiency achievable using cellulose nanofibres derived from banana fibres in a PVA matrix using different methods of

pre-treating the fibres prior to mechanical shear (routes A-C). Tensile modulus is increased by around 300% with only 5wt% addition of nanofibres.

Current work is focusing on composite preparation procedures using traditional melt compounding with polyethylene. This involves the use chemical modification procedures on the fibres to prevent nanofibre agglomeration and to aid dispersion, together with the effects of uniaxial and biaxial deformation on structure and properties of the composites with a view to their use in packaging applications.

References:

1. PR Hornsby and E Qua, Preparation and characterization of polyvinyl alcohol nanocomposites made from cellulose. *Journal of Applied Polymer Science*, **113**, 2238-2247, (2009).
2. PR Hornsby and E Qua, Preparation and characterisation of nanocellulose reinforced polyamide-6, *Plastics, Rubber and Composites* **40**, 300-306, (2011).
3. HSS Sharma, E Carmichael, M Muhamad, D McCall, F Andrews, C McRoberts, and PR Hornsby, Biorefining of perennial ryegrass for the production of nano-fibrillated cellulose, *RSC Advances*, In press (2012).

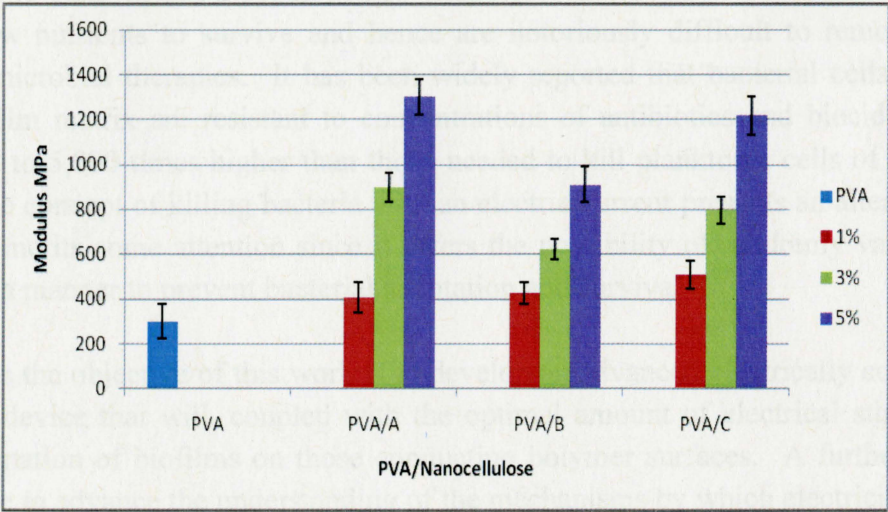


Fig.1 Tensile properties of solution cast PVA/banana cellulose nanofibre composites at 1, 3 and 5 wt% fibre addition levels.

The effect of electric current on bacterial adherence to conducting polymers

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Brendan Gilmore^b

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Introduction

A relentless clinical menace, bacterial biofilms thrive on the surfaces of indwelling medical devices (IMDs) such as urinary catheters and are responsible for about 90 percent of infections picked up the hospitals of developed countries [1]. Biofilm bacteria enter a reduced metabolic state within a sophisticated exopolysaccharide (EPS) matrix where they require very few nutrients to survive and hence are notoriously difficult to remove using traditional antimicrobial therapies. It has been widely reported that bacterial cells residing within the biofilm matrix are resistant to concentrations of antibiotics and biocides which range from 500 to 5,000 times higher than those needed to kill planktonic cells of the same species [2]. The concept of killing bacteria with an electric current presents an alternative to antibiotics that merits some attention since it offers the possibility of randomly varying the electric field in a manner to prevent bacterial adaptation and survival.

To that end, it is the objective of this work is to develop an advanced electrically conducting polymer based device that will, coupled with the optimal amount of electrical stimulation, prevent the formation of biofilms on those conducting polymer surfaces. A further project objective will be to advance the understanding of the mechanisms by which electricity affects bacterial growth.

Experimental Method

The experimental methodology utilized in this work is summarized in Figure 1. An electrified modified Robbins device was designed and built to allow application of electric current to the surface of composite conducting polymers under bacterial flow conditions akin to typical microbiological adherence assays.

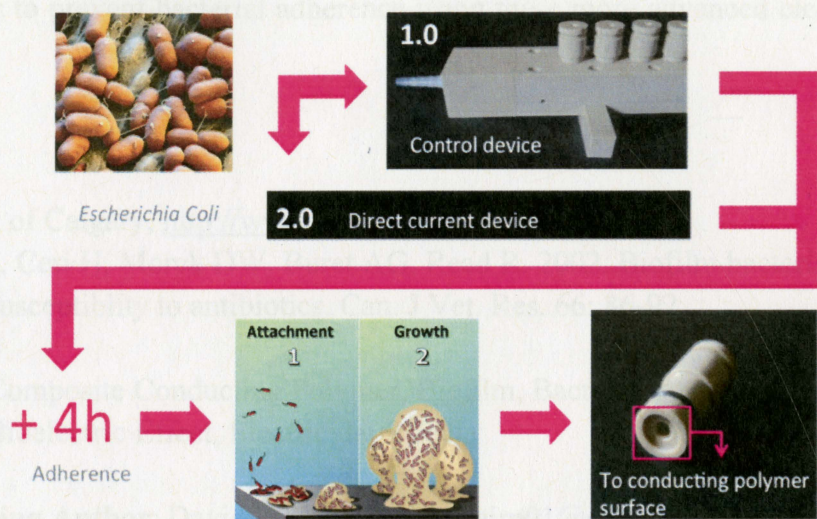


Figure 1. Experimental methodology

Results and Discussion

By Increasing Average Current		By Increasing High Current	
Average Current (mA)	CFU/disc	High Current (mA)	CFU/disc
0.0028381	2.83E+05	0.0106	2.83E+05
0.0028381	6.33E+05	0.0106	6.33E+05
0.0028381	1.42E+05	0.0106	1.42E+05
0.0028381	1.83E+04	0.0106	1.83E+04
0.0034412	5.83E+04	0.0119	5.83E+04
0.0034412	3.33E+04	0.0119	3.33E+04
0.0034412	4.33E+03	0.0119	4.33E+03
0.0034412	2.00E+04	0.0119	2.00E+04
1.5235	1.67E+04	1.7	1.67E+04
1.5235	7.67E+04	1.7	7.67E+04
1.5235	1.33E+05	1.7	1.33E+05
1.5235	1.50E+05	1.7	1.50E+05
2.0184	6.00E+05	2.62	6.00E+05
2.0184	2.00E+04	2.62	2.00E+04
2.0184	1.02E+05	2.62	1.02E+05
2.0184	5.00E+04	2.62	5.00E+04
2.7676	1.35E+05	2.91	1.35E+05
2.7676	3.42E+04	2.91	3.42E+04
2.7676	8.33E+04	2.91	8.33E+04
2.8138	4.83E+04	2.95	4.83E+04
2.8138	3.17E+04	2.95	3.17E+04
2.8138	6.83E+03	2.95	6.83E+03
2.8557	0	3.1	0
2.8557	0	3.1	0
2.8557	0	3.1	0
2.9924	0	3.38	0
2.9924	0	3.38	0
2.9924	0	3.38	0
3.7243	0	4.03	0
3.7243	0	4.03	0
3.7243	0	4.03	0
4.852	0	4.94	0
4.852	0	4.94	0
4.852	0	4.94	0

Table 1. Effect of DC electric current on the number of adhered surface bacteria in colony forming units per polymer disc (CFU/disc)

Results in Table 1 demonstrate discovery of a threshold DC current range which, when applied to the surface of conducting polymer materials within our flow device, completely halt the initial attachment of bacteria to their surfaces. Further work is already underway to develop low frequency AC and RF -modified versions of the flow device in order to unlock

the conditions to prevent bacterial adherence using these more advanced electrical treatment regimes.

References

- [1] University of Calgary, <http://www.ucalgary.ca/biofilm>
- [2] Olson ME, Ceri H, Morck DW, Buret AG, Read R. 2002. Biofilm bacteria: formation and comparative susceptibility to antibiotics. Can. J Vet. Res. 66: 86-92

Keywords: Composite Conducting Polymer, Biofilm, Bacterial Adherence, Adhesion, Initial Attachment, Bioelectric Effect, Electricidal Effect

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Figure 1. Polystyrene degradation mechanism of TiO₂/Graphene composite

Using nanomaterials in water and wastewater treatment

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^a *Dublin City University, Dublin 9, Ireland*

A number of different nanomaterials are being developed for use in water and wastewater treatment. In particular, the photocatalytic semiconductor Titanium Dioxide (TiO_2) has attracted extensive attention in recent decades and is being used in the degradation of organic pollutants such as detergents, dyes, pesticides, herbicides and pharmaceuticals in water and wastewater. A problem with using TiO_2 on its own is that it can agglomerate in water and is very hard to remove from the water after treatment. To solve this problem nano- TiO_2 can be immobilised onto a host material as a catalytic support. This has resulted in the development of Integrated Photocatalytic Adsorbents (IPCAs), typically with Activated Carbon as the host material. A promising new nanomaterial is TiO_2 nanotube (TNT), which has special electronic and mechanical properties, high photocatalytic activity, large specific surface area and high pore volume. Using such nanomaterials in water and wastewater treatment is relatively new; using TNTs in combination with Graphene is newer still. Much of the research to date has been into improving the methods of nanostructure formation by controlling the size, shape, crystal structure and surface properties and into methods to tailor the nanomaterials for a particular application as well as identifying different host materials. Mixed results using these IPCAs for pollutant removal has been reported in the literature and confirmed in our work. This presentation explores these issues and outlines developments in the area.



Figure 1. Pollutant degradation mechanism of TiO_2 /Graphene composite

Keywords: nanomaterials, water treatment, adsorption photocatalysis, integrated photocatalytic adsorbent.

***Corresponding Author:** Dr. Anne Morrissey, anne.morrissey@dcu.ie

Toxicity testing and risk assessment of new materials, chemicals and other agents are undergoing significant re-evaluation on both the manufacturing and the regulatory side of commercialization. What agents need to be tested for human and environmental impact, what are the most effective means to test a broad range of agents and what screening methods will minimize the use and cost of animals are questions driving changes in toxicology testing strategies. We now know engineered nanomaterials (ENMs) present unique challenges in toxicity assessment as their size, shape and surface chemistry alter their properties and functionalities in unanticipated ways not predicted by their bulk material equivalent. We have developed a new rapid multiplex biosensor platform termed the Nanosensor that uses human cells to screen agents including ENMs for cytotoxic and dose response analysis.

The core of the Nanosensor system is an acoustic wave device (AWD) with living cells attached to its surface. AWDs measure mass per unit area by measuring the change in frequency of a quartz crystal resonator. This cell integrated biosensor can then be used to detect specific perturbations of the cell or its internal structural elements or organelles in an automated, continuous and quantitative manner. We have shown over the last decade that the technology can be used to address several different areas of research: as a toxicity assay, a drug discovery tool and for the diagnosis and prognosis of cancer. In the current presentation the use of the Nanosensor platform for toxicity testing will be described.

Reversing an inhalation exposure or an equivalent, individual AWDs incorporating either macrophages, human pulmonary endothelial or epithelial cells were used to test lung cell responses to varying doses of carbon nanotubes or nanotubes, azide, or nanosilver, and results in the AWDs were compared to those of the same cells and agents using traditional toxicity assays including quantitative LDH release, apoptotic and cell viability assays.

Macrophages were most sensitive to nanotubes and nanosilver with AWD responses at 6 hrs accurately predicting their cell death 48-72 hrs later. In contrast, human lung endothelial cells were most sensitive to nanosilver and azide with an AWD response seen at 6 mins that was correlated to toxicity 48-72 hrs later. Epithelial cells of the lung were minimally affected by these agents in the AWD assessments or the conventional assays. Interference of traditional toxicity assays by nanomaterials and how to correct for interference will also be discussed.

1. Wang Q, Zhang L, Brown AM, Pei X, Sato H, Thorne SA, Bawole SO, Wang L, Li J. 2011. Understanding and controlling the cellular uptake of carbon nanotubes with a commercial LDH cytotoxicity assay. *Toxicology* 280:104-114.
2. Wang Q, Wang L, Brown AM, Sato H, Thorne SA, Bawole SO, Wang L, Li J. 2011. Carbon nanotubes and nanotubes: different agents, different cellular uptake mechanisms with varying rates of cell death. *Applied Bioscience* 2:165-171.
3. Wang Q, Brown AM, Wang L, Li J, Wang M, Sato H, Wang KA, Thorne SA, Bawole SO, Wang L. 2011. A novel cell-based assay for nanotoxicity assessment for nanomaterials. *Journal of Cellular Biochemistry* 119:104-114.

Key words: acoustic wave devices, quartz crystal microbalance, toxicity testing, carbon nanotubes, carbon nanotubes, pulmonary endothelial cells, macrophages, nanosilver.

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Nanocanary™ Technologies: Cell-based biosensors to evaluate cellular response to nanomaterials, chemicals, drugs and toxins.

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Toxicity testing and risk assessment of new materials, chemicals and other agents are undergoing significant re-evaluation on both the manufacturing and the regulatory side of commercialization. What agents need to be tested for human and environmental impact, what are the most effective means to test a broad range of agents and what screening methods will minimize the use and cost of animals are questions driving changes in toxicology testing strategies. We now know engineered nanomaterials (ENMs) present unique challenges to toxicity assessment as their size, shape, and surface chemistries alter their properties and functionalities in unanticipated ways not predicted by their bulk material equivalent. We have developed a new rapid multiplex biosensor platform termed the *Nanocanary* that uses human cells to screen agents including ENMs for biohazard and dose response analysis.

The core of the *Nanocanary* system is an acoustic wave device (AWD) with living cells attached to its surface. AWDs measure mass per unit area by measuring the change in frequency of a quartz crystal resonator. This cell integrated biosensor can then be used to detect specific perturbations of the cell or its internal structural elements or organelles in an automated, continuous and quantitative manner. We have shown over the last decade that the technology can be used to address several different areas of research: as a toxicity assay, a drug discovery tool and for the diagnosis and prognosis of cancer. In the current presentation the use of the *Nanocanary* platform for toxicity testing will be described.

Representing an inhalation exposure organ simulant, individual AWDs incorporating either macrophages, human pulmonary endothelial or epithelial cells were used to test lung cell responses to varying doses of carbon nanotubes or nanohorns; azide; or nanosilver, and results in the AWDs were compared to those of the same cells and agents using traditional toxicity assays including quantitative LDH release, apoptotic and cell viability assays.

Macrophages were most sensitive to nanotubes and nanohorns with AWD responses at 6 hrs accurately predicting their cell death 48-72 hrs later. In contrast, human lung endothelial cells were most sensitive to nanosilver and azide with an AWD response seen at 6 mins that was correlated to toxicity 48-72 hrs later. Epithelial cells of the lung were minimally affected by these agents in the AWD assessments or the conventional assays. Interference of traditional toxicity assays by nanomaterials and how to correct this interference will also be discussed.

1] Wang G, Zhang J, Dewilde AH, Pal AK, Bello D, Therrien JM, Braunhut SJ, Marx KA. 2012. Understanding and correcting for carbon nanotube interferences with a commercial LDH cytotoxicity assay. *Toxicology*. 299:99-111.

2] Zhou T, Marx KA, Dewilde AH, McIntosh D, Braunhut SJ. 2012. Dynamic cell adhesion and viscoelastic signatures distinguish normal from malignant human mammary cells using quartz crystal microbalance. *Analytical Biochem*. 421:164-71.

3] Wang G, Dewilde AH, Zhang J, Pal A, Vashist M, Bello D, Marx KA, Braunhut SJ, Therrien JM. 2011. A living cell quartz crystal microbalance biosensor for continuous monitoring of cytotoxic responses of macrophages to single-walled carbon nanotubes. *Part Fibre Toxicol*. 8:4.

Key words: acoustic wave devices, quartz crystal microbalance, toxicity testing, carbon nanotubes, carbon nanohorns, pulmonary endothelial cells, macrophages, nanosilver.

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Biodegradable Polymers for Medical Applications

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Poly(lactic acid) or polylactide polymers have been successfully utilized as medical implants due to their biocompatibility with biological tissues, degradability *in vitro* and *in vivo*, and good mechanical properties. Extensive work has been carried out by several investigators in understanding the morphological properties of polylactide (poly(lactic acid) PLLA). In particular, considerable progress has been made in elucidating the crystalline structure and crystallization kinetics of PLLA. Recently, detailed studies were carried out to investigate the influence of physical aging on the viscoelastic behavior of PLLA, and the effects of water sorption on the thermal motions in PLLA and other related polymers. The influence of morphology (crystalline and amorphous) on the degradation of PLLA was conducted in aqueous media for periods up to 2 years. It was found from this study that the highly crystalline regions appear to be very resistant to degradation and that degradation proceeds more rapidly in the amorphous than in the crystalline regions. Both the crystalline and amorphous regions.

Session 3

Medical Devices/Biomaterials

Chair: Professor Eileen Harkin-Jones

Dramatic effects of polymer architecture and the resulting crystalline morphology on enzymatic degradation of poly(l-hydroxybutyrate) and PLA have been studied extensively in our laboratory. The effects of polymer architecture on the degradation of PLA and PLA blends have been studied in our laboratory. The results of this work have been published in the literature and will have a great impact in interpreting the degradation behavior of PLA and PLA blends in various applications.

Biodegradable hollow nanospheres have been constructed by assembling block copolymers of various biodegradable polymers. These spheres are less than 50 nm in diameter, with hollow cores, and are constructed of biodegradable polymers. The core can be filled with various drugs for drug delivery. The nanospheres have been shown to enhance the efficiency of drug delivery through the skin and into the blood stream. This also allows more efficient delivery of drugs. In addition these nanospheres are able to protect the drug from degradation in the blood stream. The primary components of the biodegradable shell are polylactides such as polylactide, which are safe to consume.

The nanospheres are less than 50 nm in diameter and are manufactured using a special manufacturing process. Potential applications include wound healing, cell delivery, drug delivery, and gene delivery.

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Biodegradable Polymers for Medical Applications

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Poly(lactic acid) or polylactide polymers have been successfully utilized as medical implants due to their biocompatibility with biological tissues; degradability *in vitro* and *in vivo*; and good mechanical properties. Extensive work has been carried out by several investigators in understanding the morphological properties of poly(L-lactic acid) [PLLA]. In particular, considerable progress has been made in elucidating the crystalline structure and crystallization kinetics of PLLA. Recently, detailed studies were carried out to investigate the influence of physical aging on the viscoelastic behavior of PLLA, and the effects of water sorption on the internal motions in PLLA and other related polymers. The influence of morphology (crystalline and amorphous) on the degradation of PLLA was conducted in aqueous media for periods up to 2 years. It was determined from this study that the highly crystalline residues appear to be very resistant to degradation, and that degradation proceeds more rapidly in the center than at the surface for both the crystalline and the amorphous specimens.

Dramatic effects of polymer stereochemistry and the resulting crystalline morphology on enzymatic degradation of poly(β -hydroxybutyrate) and PLA have been studied extensively in our laboratory. The importance of morphology on degradation has been established for PLA and a more detailed treatise on this subject is needed as the information generated will have a great impact in interpreting the degradation behavior of PLA prepared from different processing techniques for various applications.

Biodegradable Hollow Nanospheres have been constructed by assembling linear block copolymers of various biodegradable polymers. These spheres are less than 50 nm in diameter, with hollow cores, and are constructed of biodegradable polymers. The core can be filled with various drugs for drug delivery. The nanospheres have been shown to enhance transdermal drug delivery through the skin of mice and into the blood stream. This also allows more efficient delivery of drugs. In addition these nanospheres are able to protect insulin from stomach acids so that diabetics can take insulin orally. The primary components of the biodegradable shell are polysaccharides such as pullulan, which are safe to consume.

Silk Nanofibers are less than 50 nm in diameter and are manufactured using a special electrospinning process. Potential applications include wound healing scaffold for burns.

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Bioresorbable Implants for Orthopaedic Applications

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Keywords: bioresorbable, polymer, irradiation, controlled release

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Introduction

Bioresorbable polymeric devices are being increasingly used in fixation of bone fractures, where they are gradually resorbed by the body and replaced by new bone. They avoid long-term complications including pain and secondary surgical retrieval procedures associated with metal implants. This work has focused on an electron beam treatment to modify polymer surface degradation for controlled release of bioactive components.

Experimental methods

Prototype ACL screws produced from poly(lactic-co-glycolic acid) (PLGA) containing a calcium phosphate filler were supplied by Smith & Nephew (Mansfield, USA). Electron-beam irradiation was carried out at Risø DTU, Denmark using a beam energy of 125 keV with delivered doses of 150 kGy and 500 kGy. Screws were subjected to an accelerated hydrolytic degradation treatment (47°C, for up to 17 days) and monitored by mass loss and scanning electron microscopy (SEM). Release rate of calcium ions was monitored by inductively coupled plasma mass spectrometry (ICP-MS).

Results and discussion

Weight loss after accelerated degradation was relatively small, however SEM micrographs confirmed that there was significant surface degradation of the irradiated screws. Figure 1 shows relatively high levels of calcium ion release from the irradiated screws in comparison to the non-irradiated controls. This would suggest that the enhanced surface degradation of the irradiated screws is promoting dissolution of calcium phosphate.

Conclusion

Manipulation of the surface-to-core degradation profile may have benefits in terms of *in vivo* performance, with early release of calcium being demonstrated in this study. These ions are considered bioactive and play an important role in the bone healing process. This work has illustrated the potential of electron beam technology in achieving a depth-dependent degradation rate and ultimately improved bioresorbable medical devices.

Acknowledgements

Risø DTU, Denmark for the irradiation treatments. UK Dept. of Health (HTD409), Synergy Health and Smith & Nephew for funding.

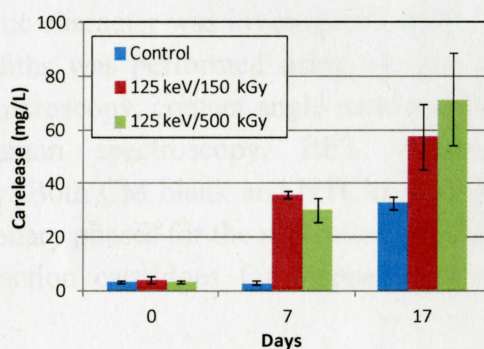


Figure 1. Calcium ion concentration in degradation medium after 7 and 17 days

Porous nano-templated carbon monolithic structures and associated fabrication effects from laser ablation

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Abstract

In recent years, there is a growing interest to the synthesis of a bimodal interconnected meso- and macroporous carbon materials, which are widely used in adsorbents, water purification, energy storage, catalyst supports and chromatography. The aim of this work was the development and characterisation of novel carbonaceous monolithic stationary phases which have unique selectivity and high adsorption capacity for uses in chromatographic and solid phase extraction sorbents. A blank carbon monolith (CM blank) was prepared using a bare silica template. The preparation of nano-templated carbon monoliths (NTCM) using C60-fullerene modified silica gels (denoted as FMS) was undertaken and the resulting new chromatographic materials fully characterised using various physical and chemical techniques and investigated the chromatographic applications. The FMS template materials were fully characterised to confirm the covalent bond between C60 and the primary amine of 3-aminopropyl silica (APS). Using FMS as template C60 was consequently introduced into the macroporous wall structure of the monolith and the effect of this upon final monolith structure, specific surface area and overall graphitic character was investigated. In particular, detailed characterisation of all fabricated monoliths was performed using various physico-chemical techniques, namely scanning electron microscopy, contact angle measurements for hydrophobicity estimation, ATR-IR and Raman spectroscopy, BET surface area measurements and mercury intrusion porosimetry. Both CM blank and NTCM were applied as electrode modifier in cyclic voltammetry, stationary phases for the separation of phenols in reversed-phase HPLC, and as solid-phase extraction cartridges for bisphenol A and its derivatives.

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Injectable Orthopaedic Bone Cements: Advanced Mixing and Delivery

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Surgical implantation of a cemented hip prosthesis is a difficult procedure. Failure can take place at the cement-implant interface, within the cement mantle or the bone-cement interface. In the case of the cement mantle, the basis for using cement mixing methodologies that reduce air bubbles in the cement is logical and is well supported by many experimental studies. On the basis of the Swedish Hip Register it has been calculated that the use of vacuum mixed bone cement lowers the risk of aseptic loosening in the mid- to long-term follow-up. However, no clinical outcome studies have been published in which the mixing technique and cement porosity were evaluated; therefore the clinical relevance or reduction in porosity has been questioned.

In a previous study of third generation techniques using proprietary cement mixing and delivery devices, we evaluated the quality of bone cement produced by 35 different theatre scrub staff during the course of actual hip replacement procedures at an orthopaedic hospital. The study concluded that the cement quality was improved when prepared using vacuum mixing techniques in comparison to cement prepared under atmospheric conditions. However, the cement mixed under vacuum still produced cement of variable porosity with the consequence that the quality was often less than ideal, the mean porosity values ranging between 1.24 % and 12.90 %. Therefore suggesting that current bone cement mixing technology is not wholly operator independent as the quality of the cement mix is unreliable and inconsistent.

In this paper, we will demonstrate the cement quality produced using an innovative, operator independent mixing and delivery system that has been developed in our research group. Its efficacy will be determined via comparison with different proprietary mixing system currently in used in Europe and the USA.

Keywords: PMMA bone cement, mixing, orthopaedic surgery

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Biomedical Diagnostics: Challenges and Recent Advances

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The **Biomedical Diagnostics Institute (BDI)** is a Science Foundation Ireland funded CSET (Centre for Science, Engineering and Technology). Originally established in October 2005, the BDI is an Academic-Industrial-Clinical partnership that carries out cutting-edge research focused on the development of next-generation biomedical diagnostic devices. Its vision is to transform healthcare by pioneering advances in the science and technology of diagnostics and by translating these advances into clinical use.

The Biomedical Diagnostics Institute is an integrated multidisciplinary research institute focused on the development of next generation 'point-of-care' biomedical diagnostics and associated devices working in close association with Irish and global industries.

In addition, it is focused on providing insights into its research for decision makers and the general public, for improving patient care and for generating highly skilled personnel through its research and through its Masters and associated degree programmes.

Having pioneered advances in fundamental diagnostic technologies from our established core competencies in our first 5 years, our clear goal is to translate novel diagnostic devices into clinical and commercial reality. BDI research strands address major clinical challenges informed by the partnership of clinicians, scientists and industry. Building on key scientific insights, the BDI is now applying its established capabilities to create integrated 'point-of-care' solutions, which will have major impacts on diagnosing disease and sustaining human health. It is also developing novel approaches, reagents and platforms that offer significant improvements over current methods.

An overview of the capabilities and partners of the BDI will be given, and key areas of research linked to major challenges in the area of biomedical diagnostics will be discussed.

Keywords: Biomedical Diagnostics, Point-of Care.

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NOTES:

Queen's University Belfast

Campus Map

